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EPR Studies on Mn-Doped SnTe Crystals (III)

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The paramagnetic resonance has been studied on Mn^{2+} ions (<0.5 atm%) diluted in the degenerate semiconductor SnTe crystals with low carrier concentration ($p=1.2-2\times10^{20}cm^{-3}$) prepared by annealing the as-grown crystals in Zn vapor at 600°C for two days. To see the influence of free carriers on the magnetic ions in this material we observed the change in the linewidth ΔH with Mn content and temperatures between 120 and 480 K. As a result, an exchange narrowing effect was found to be effective; the decrease in ΔH with increasing temperature is closely related with that in the carrier concentration, which is based on the electron transfer between the two-valence bands of SnTe. The hyperfine interaction constant was found to be 56×10^{-4} cm^{-1} comparable with that of CdTe. The susceptibility measurements of the samples with 0.88 and 2.2 atm% Mn in the range 77−300 K are also presented to show some magnetic inclusions in the grown crystals.

1. Introduction

Narrow-gap semiconductors and their mixed crystals as well are of current interest with respect to the band structure, phase transition and industrial application.[1,2] Thus far we have been concerned with the studies of the interaction between free carriers and magnetic impurities in the degenerate semiconductor SnTe with the two-valence bands from both transport[3] and spin resonance experiments.[4,5] All samples used previously for the spin resonance were prepared by annealing the Bridgeman-grown SnTe crystals in Sn-vapor at 500°C for two days and the resulting nominal carrier concentrations p calculated from the Hall coefficient were in the range $4-8\times10^{20}cm^{-3}$. The experimental results have shown that, (i) the width of a broadened line increases linearly with the nominal Mn content up to 0.05 atm% caused by a dipolar interaction, (ii) a saturation behavior of ΔH for higher Mn content indicating the incomplete solubility of Mn atoms in the host, and (iii) there may be some contribution from motional and exchange narrowing effect to the linewidth.

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Furthermore, we have pointed out from the electrical measurements[3,6] that higher carrier concentrations than $p_k=2-3\times10^{20}cm^{-3}$ make the effect of magnetic ions obscure through a charge screening. In view of the characteristic band structure of SnTe with two-valence bands, the charge carriers would be preferable to be reduced down to less than a critical concentration p_k, which characterizes the carrier population between the light-mass hole and heavy-mass hole bands. In this work we have used the samples with less carrier concentrations prepared by annealing the as-grown crystal in Zn-vapor at 600°C for two days. Here the emphasis is to be placed on the comparison of the data between the samples with higher concentration ($p=4-8\times10^{20}$ cm^{-3}) and those with lower concentration ($p=1.2-2\times10^{20}cm^{-3}$). The susceptibility measurements carried out by Dr. M. Nomura of Hiroshima University on our samples with 0.88 and 2.2 atm% Mn are also presented to see some possibility of existence of magnetic inclusions in the grown crystals.

2. Experimental Results and Discussions

The method of preparation of all the samples has been described previously.[3-6] The essential point to be noted is to anneal the as-grown crystals in Zn-vapor at 600°C for two days, the resulting carrier concentration being in the range $p=1.2-2\times10^{20}cm^{-3}$ estimated from the Hall coefficient at room temperature;[6] in this work the nominal Mn content is expressed in atomic percent instead of weight percent used thus far. Figure 1 represents the linewidth ΔH of present samples against the Mn content at room temperature, while the dotted line shows the previous data with high carrier concentration ($p=4-8\times10^{20}cm^{-3}$). A marked difference can be seen between the two results; the linewidth is almost independent of the amount of Mn ions up to 1 atm%, while it increases with Mn content for higher content that 1 atm%. We note that the absolute value of ΔH is smaller than the previous linewidth at least for samples with Mn<2 atm%; in other words, free carriers are responsible for the EPR linewidth of Mn^{2+} ions in SnTe.

One of the characteristic features of the present samples is the fact that for low Mn content less than 0.3 atm% the five-line hyperfine structure is resolved even at room temperature with reproducibility, whereas in the case of the previous work the HFS-line was rarely observed and even if it happened to appear at room temperature, it disappeared after a heat-cycle between 120 and 480K. The typical signals observed at 120 K are illustrated

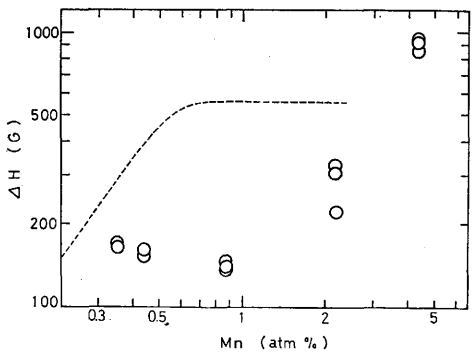

Fig. 1 EPR linewidth ΔH of Mn^{2+} ion in SnTe vs nominal Mn content at room temperature. The dotted curve shows the data taken previously.[4,5]

in Fig. 2 for two samples with 0.22 atm% and 0.04 atm% Mn.

The six lines can be fit by the Hamiltonian

$$\mathcal{H}=g\beta \boldsymbol{H}\boldsymbol{S}+\boldsymbol{A}\boldsymbol{I}\boldsymbol{S}. \qquad \cdots\cdots(1)$$

The g value was found to be nearly equal to 2. The temperature dependence of the hyperfine constant A of Mn^{2+} (0.04 atm%) in SnTe was for the first time measured by us, as shown in Fig. 3 in the two units (Gauss and cm^{-1}). It can be approximately represented by $A(T)=A-BT$ (A,B=constant) as in II-VI semiconductor;[7] the constant $A(T)$ increases as the temperature is lowered and tends to level off at temperature lower than, roughly speaking, the Debye temperature θ_D. From Fig. 3 we estimate θ_D of SnTe to be in the range 150—200 K.

The values of A are known to represent the scale of ionicity and covalency of the host crystal, as reviewed in ref.8. In Table I are summarized the values of A, lattice constant a and Debye temperature for some IV-VI semiconductors. As noted by Pifer,[9] the lead salts are quite covalent, and it is likely that SnTe with a NaCl

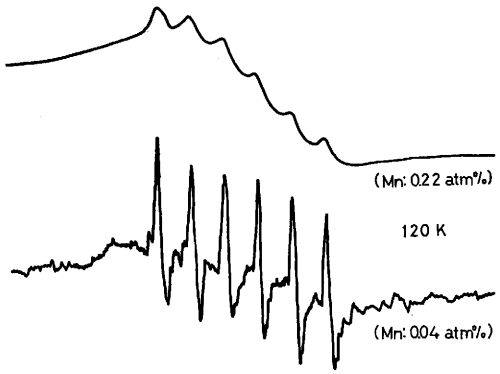

Fig. 2 Hyperfine structure observed at 120 K for two samples with 0.22 atm% and 0.04 atm% Mn in SnTe.

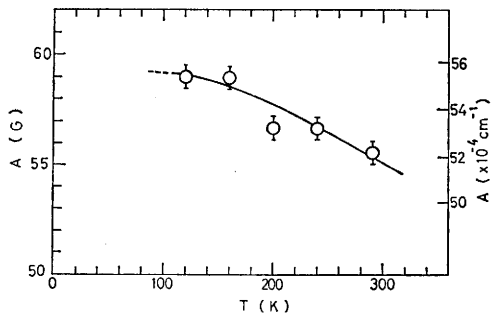

Fig. 3 Temperature dependence of the hyperfine interaction constant A of Mn^{2+} (0.04 atm%) in SnTe crystals with carrier concentration $1.2-2\times10^{20}$ cm^{-3}.

Table I. Comparison of the hyperfine interaction constant A, lattice costant a and Debye temperature θ_D of some IV-VI semiconductors.

Material	A ($\times10^{-4}cm^{-1}$)	Temperature (K)	a** (Å)	θ_D*** (K)
PbS	71.8*	1.3	5.936	195
PbSe	67.6*	1.3	6.124	135—160
PbTe	61.2*	1.3	6.454	124—135
SnTe	56+	120	6.313	150—200+

*) ref. 9.

**) R. C. Weast ed.: *CRC Handbook of Chemistry and Physics* (Chemical Rubber Co., Cleveland) 51st Ed.

***) *American Institute of Physics Handbook* (McGraw-Hill, N. Y., 1972) 3rd Ed.

+) Present work (Submitted to Phys. Letters).

crystal structure is more covalent, the value A of SnTe being comparable with that of CdTe (A=57.1×10^{-4}cm^{-1} for hexagonal structure)[10]. However, Urban and Sperlich[11] have assigned the well-known covalency scale c/n (the covalency c divided by the number of ligands n) to be about 13.8% from the value A of Eu in SnTe. These considerations can be seen more clearly from the A(Mn^{2+}) vs c/n relation, as demonstrated in Fig. 4. If we cite c/n=13.8 % for SnTe, the constant A would become much larger (those of MgS, CaSe and MgSe) in contrast with the present value of A. It is to be noted further that recent theoretical and experimental studies predict a softening of the TO phonon with decreasing temperatures in IV-VI semiconductor, accompanying with a phase transition NaCl→rhombohedral structure. Then the hyperfine constant A may also vary with temperature under the phase transition, since it depends on the crystal structure. Although the present results of Fig. 3 is too rough to predict the transition temperature, more careful measurement of the constant A could probably uncover this possibility.

The temperature dependence of the linewidth ΔH is shown in Fig. 5 for some samples with different Mn contents. The activation energies observed in a certain temperature range are indicated for respective samples, according to a relation $\Delta H \propto \exp(\varepsilon/kT)$; these energies ε are of the order of $1-3\times10^{-2}$eV. The figure also shows that the linewidth become almost temperature-independent at low and high temperatures. On the level-off of ΔH with T at low temperatures, we have previously[5] speculated that it may be due to incomplete solubility of Mn atoms into SnTe or the presence of some magnetic

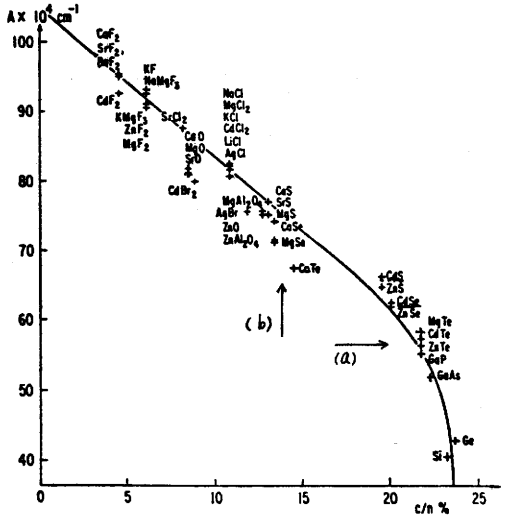

Fig. 4 Hyperfine constants A of Mn^{2+} ions in various host crystal vs. c/n [after E. Simánek and K. A. Müller: J. Phys. Chem. Solids 31 (1970) 1027]. An arrow (a) indicates the A-value of SnTe determined from this work and the one (b) the corresponding value of c/n of Eu in SnTe taken from Fig. 2 of ref. 11.

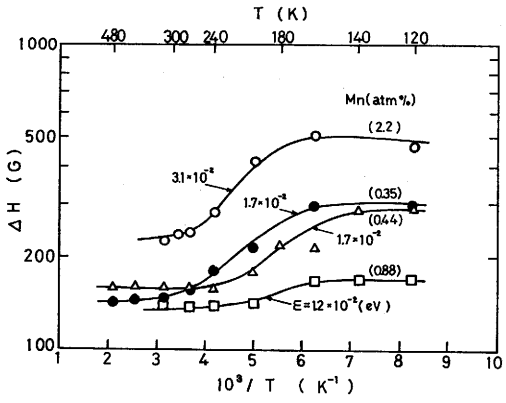

Fig. 5 Temperature dependence of the EPR linewidth for samples with different Mn content. The activation energies ε for the respective slopes are indicated in eV unit.

materials such as of ferro-, antiferro-and ferri-magnetic nature; these can be clarified by a susceptibility measurement.

Fig. 6 shows the results of the susceptibility as a function of temperature for some samples with 0.88 and 2.2 atm% Mn in the range 300−77 K; the measurements were carried out by Dr. M. Nomura of Prof. H. Fujiwara group (Hiroshima Univ.). The sensitivity of the magnetic balancs was checked by the Mohr's salt, $FeSO_4$ $(NH_4)_2$ $SO_4 \cdot 6H_2O$. These curves were obtained for the samples cut independently from the different grown-ingots. The $1/\chi - T$ curves are seen to be different in its behavior even for the samples with the same amount of Mn (2.2 atm%) ; the one has a paramagnetic Curie temparature of about 10 K, while the other shows a knik at 145 K and the $1/\chi$ value vanishes at −9.5 K. The curve for 0.88 atm % Mn has also a knik at 183 K and its value of $1/\chi$ is extrapolated to zero at temperature of 40 K. Although experimental data of the susceptibility are limited, we may speculate from these results that the magnetic Mn impurities are not always dissolved homogeneously into the host crystal (*i. e.*, incomplete solubility of Mn atoms), as already pointed out previously.[5] Furthermore, the knik observed in the $1/\chi - T$ curve would suggest the formation of some clusters of Mn atoms with neighboring Sn and/or Te atoms, namely the presence of some magnetic materials with the Curie or Néel temperature of approximately 145−180 K; the identification of any possible magnetic inclusions is still uncertain from the limited data. The presence of a ferromagnet or antiferromagnet would give rise to a shift of the resonance curve, though our observed EPR lines are at present difficult to be analyzed.

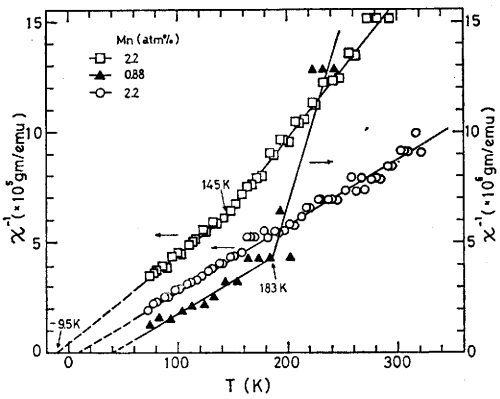

Fig. 6 Temperature dependence of reciprocal susceptibility of SnTe, measured by Dr. M. Nomura (Hiroshima Univ.).

In conclusion, we have carried out the EPR measurements on Mn^{2+} ions diluted in the degenerate semiconductor SnTe grown by the Bridgeman technique. In the studies of both transport and spin resonance for this material, one must note the carrier concentration involved; the present samples were annealed in Zn-vapor at 600°C for two days and the resultant concentrations were in the range $1.2-2\times10^{20}$ cm^{-3}, whereas in the previous work the heat-treatment was made in Sn-vapor at 500°C, the concentration being $4-8\times10^{20}cm^{-3}$. The characteristic features obtained in this work are summarized as follows: (a) The EPR linewidth is narrower for the samples with less carrier concentrations than those with higher concentrations (see Fig. 1). This is one of the most important results; in effect we may express that the free carriers are responsible for the linewidth in the SnTe crystals. (b) In

addition, the temperature dependence of the width is closely related with the variation of the free carriers (Fig. 5), which is characteristic of the semiconductor, in particular SnTe having two-valence bands. This characterizes a marked difference against the magnetic dilute alloys (metal). (c) The HFS lines observed in the present samples with 0.04 atm% Mn have revealed that the electronic nature of chemical bonding in this host material is more covalent than one may imagine from its crystal structure of a cubic NaCl type (the hyperfine interaction constant $A = 56 \times 10^{-4}\mathrm{cm}^{-1}$); most of the crystals with NaCl structure have a coordination number of six and are ionic in chemical nature. (d) It is likely that the Mn ions are not dissolved homogeneously in the host, but rather they tend to form clusters with the neighbouring host elements Sn and Te, resulting in the precipitates of some magnetic materials, as revealed from the susceptibility measurements on the samples with higher content of Mn atoms.

From these results together with the previous data[4,5] we may state that the main contributions to the EPR linewidth of Mn-doped SnTe with the localized magnetic moments are due to the interactions between these moments (dipole-dipole and exchange interacti ns), with the conduction carriers (the Korringa mechanism), and with the inhomegeneities of the crystal lattice. It can be considered that the narrowing of the line in the samples is the consequence of indirect exchange via the conduction carriers in accordance with the RKKY (Ruderman-Kittel-Kasuya-Yoshida) theory. The overall discussions on our results can be made along with the extensive EPR investigations of Mn in copper (dilute alloys)[12,13] and magnetic Er impurity in superconducting La:[14] In the case of dilute alloys it has been recognized that there are marked effects of the exchange interaction between the $3d^5$ ion core electrons of the Mn atoms and $4s$ conduction electrons of the host crystal. The main conclusions are given of (i) the ferromagnetic coupling between Mn ions through an indirect exchange coupling via the conduction electrons, (ii) electronic Knight shift of the spin resonance line, (iii) nuclear Knight shift of the copper nuclear resonance, and (iv) electron spin relaxation by the coupling with the conduction electrons. More detailed analysis of our data will give us information stated above. However, we must note a marked difference between metal and degenerate semiconductor as a host matrix, as frequently mentioned.

Acknowledgments

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